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Creation, Categorization and Application of Metal Organic Framework of Zirconium Benzene-1,4-Dicarboxylic Acid in Adsorption of Crude Oil

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ABSTRACT

Zr-BDA was made by reacting benzene-1,4-dicarboxylic acid with zirconium chloride ($ZrCl_4$) using the solvothermal technique. The structure of the synthesized MOF was examined using energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). It was discovered that the resulting MOF had a high degree of crystallinity and surface area. The Zr-MOF's FTIR spectrum showed the presence of many functional groups as well as the potential development of a brand-new group. Comparing the new functional group to the pure spectrum of benzene-1,4-dicarboxylic acid reveals the creation of the MOF. Functional groups such as C-H, C-O, O-H, C=C, and metal-oxygen were noted. Adsorption tests revealed Zr-BDA has a 70% efficiency, which is neither appropriate nor advised. However, composites with charcoal and pH enhanced Zr-BDA's adsorptive capabilities for the crude oil.

Keywords: Zirconium benzene-1,4-dicarboxylic, Adsorption, MOF, Crude oil

INTRODUCTION

According to Zhou, Long, and Yaghi (2012), Metal-Organic Frameworks (MOFs) are enlarged three-dimensional builds of organic molecules and ions that have several places for bond formation. According to Furukawa *et al.* (2010), synthesis of transition and lanthanide metal ions with a variety of coordination geometries and organic linkers can result in a number of metal-organic frameworks. By using a range of chemical additives and a mechanochemical process, Katalin *et al.* (2021) created nanocomposites of nickel-copper-tin (dimetallics and trimetallics). Dinuclear complexes of cobalt and nickel metal-organic frameworks were created by Xiaoli, Rongli, and Feng (2021), and they were described and subjected to magnetic property investigations. They presented a finding that showed double and triple complexes to have mild antiferromagnetism. Linjian, Fangqin, and Liangfei (2018) discussed the issue brought on by the growing greenhouse effect and how more people are becoming aware of CO_2 capture and storage technologies. The details, production, and application of metal-organic frameworks in the sorption and sequestration of CO_2 were covered by Linjian *et al.* (2018) in their study, with a focus on the use of flue gas environments in power plants. Orodu and Dikio (2021) by simulating a spillage with 50 mL of distilled water, a crude oil adsorption investigation was conducted using synthesized Cu-MOF. The findings demonstrated that Cu-MOFs is a powerful adsorbent for crude oil.

Metal-organic frameworks (MOFs) are organic-inorganic hybrid crystalline porous materials that consist of a regular array of positively charged metal ions surrounded by organic 'linker' molecules (Li *et al*., 1999). The metal ions form nodes that bind the arms of the linkers together to form a repeating, cage-like structure.

Due to this hollow structure, MOFs possess an extraordinarily large internal surface area. (Li *et al.,* 1999).

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More formally, Metal–organic frameworks (MOFs) are a class of compounds consisting of metal ions or clusters coordinated to organic ligands to form one-, two-, or three-dimensional structures. They are a subclass of coordination polymers, with the special feature that they are often porous. The organic ligands included are sometimes referred to as "struts".

An example of such struts is BDA; 1,4-Benzenedicarboxylic acid

Ryder and Tan in 2014 reviewed various applications of MOFs. Some MOFs in particular were used in photolytic hydrogen production. The porous structure of MOFs also is also considered as an electrolyte membrane that can enable charge transfer from cathode to anode in fuel cells. Li *et al*. (2014) discovered an impressive property of MOFs for their medical application in that they are able to absorb and desorb drugs. Due to large surface area, it is possible to use them for gas therapy in medicine for example for N_2O delivery. Li *et al*. (2014) synthesized the HKUST-1 in a solution containing palladium Nano particles. It was found out that hydrogen gas adsorption of the resulting buildup was 74% higher than the regular palladium Nano particles. Hydrogen intake rate was also magnified by the MOF coating of the Pd Nano particles.

Several MOFs and a benchmark-activated carbon sample were studied as adsorbents to separate low-concentration Xe and Kr from air (Furukawa *et al.,* 2008). Both the Ni/DOBDC and the HKUST-1 can selectively adsorb Xe and Kr from air, even at concentrations at the parts-per-million level. The strong unsaturated metal centers in the crystal structures of the Ni/DOBDC are primarily responsible for the excellent Xe/Kr selectivity. Additionally, it is thought that the Ni/DOBDC's homogeneous cylindrical pores will help to enhance the Xe/Kr selectivity (Sikora *et al.*, 2012).

It will be easier to evaluate MOFs for sorption, separation-related applications, and selective single-component sorption and separation applications since they have demonstrated strong application potential in the field of gas capture and separations.

MATERIALS AND METHODS

Materials

Materials used in this synthesis includes Refluxer, thermometer, Magnetic stirrer, Magnetic heating mantle, Methanol, Dimethyl formamide, Benzene-1,4-dicarboxylic acid, Zirconium (IV) Chloride, Centrifuge, Electronic weighing balance, Heating oven, X ray Diffraction (XRD), Scanning Electron microscopy (SEM), Fourier Transform Infrared (FTIR).

Methods

Solvothermal method

Solvothermal synthesis of zirconium MOFs was carried out. Using an analytical weighing scale, 3.88 g of zirconium (IV) chloride ($ZrCl_4$) salt and 1.6613 g of BDA were added to the flask with a circular bottom. The round-bottom flask was additionally filled with 50 mL of the solvent, DMF. The reactants were refluxed in the electromagnetic heating mantle at 87^0C for 25 minutes while stirring was taking place with the aid of the magnetic stirrer. Within the reaction time, the solution turned from a colourless solution to a thick white precipitate. The solution at the end of the solvothermal heating process was centrifuged at 4000 rpm for 20 minutes and then washed severally with methanol. It was then oven-dried. The resultant MOF was then taken for characterization.

Characterization of the synthesized MOFs

Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) were used to characterize the MOFs as-synthesized (Figure 1).

Figure 1: (a) Fourier transform infrared spectroscopy; (b) Scanning electron microscope; (c) Energy dispersive X-ray spectroscopy

Adsorption Studies

The application of synthesized MOFs in the adsorption of petroleum waste (crude oil waste) from aqueous solutions is below.

Adsorption Procedures (Experimental)

Its capacity to absorb crude oil was assessed. The following tools were used: a conical flask, separating funnel, measuring cylinder, reciprocating stirrer, and a 10 mL pipette. For the adsorbent dosage investigation, 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g of MOF were weighed and put to separate conical flasks with distilled water to the 50 mL mark. Then it was followed by the addition of 1 mL of crude oil. After that, the mixture was stirred for a further 30 minutes. The composite was made by weighing MOF/clay and MOF/charcoal in a 50-50 ratio, i.e., 0.1/0.1 to produce 0.2 g, and so on. This was accomplished by varying the crude oil volume between 1.0, 2.0, 3.0, and 4.0 mL. We used 1.0 g each of clay, charcoal, and MOF. The effects of pH on adsorption were tested using pH values of 4.4, 6.85, and 9.0.

RESULTS AND DISCUSSION

Results

The formation of the metal-organic framework by the interaction of the chloride salts of Zirconium metal with benzene-1,4-dicarboxylic acid may be compared to a polymerization reaction where the monomers are the linkers, benzene-1,4-dicarboxylic acid, and the metal ions. The resulting structure is a chain of repeated metal atoms in the center location, with the metal ions substituting for the replaceable hydrogens in the linkers. For the adsorption procedures we will be using it in, we anticipate the material to have sufficient surface area and pores. Figure 2, is showing the dried zirconium MOFs which is white. Figure 3, is the possible structure of the Zirconium MOFs produced.

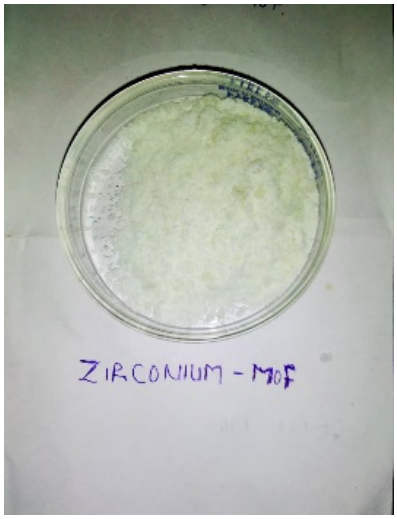

Figure 2: Zr MOF

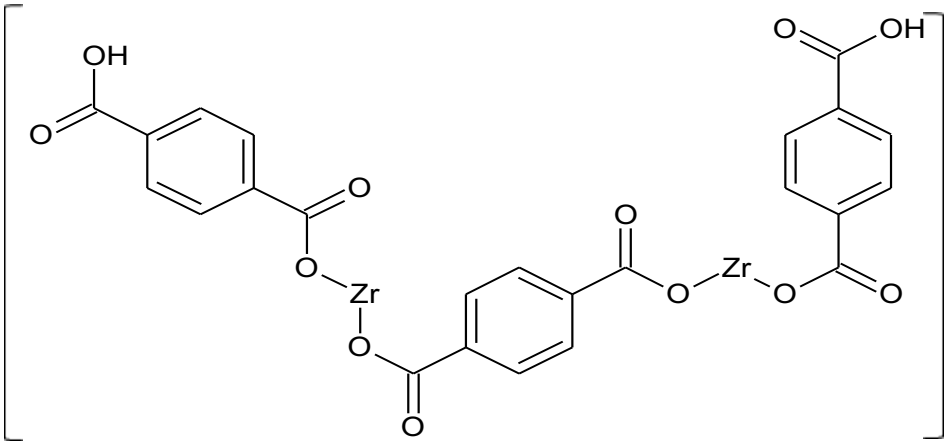

Figure 3: Zr-MOF possible bonding and repeating units in Zirconium organic

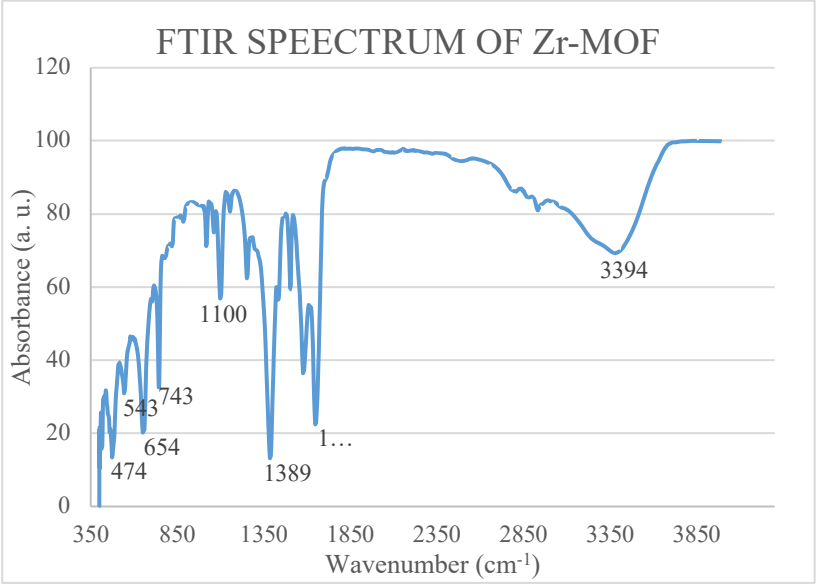

Figure 4a: FTIR Spectrum of Zr-MOF

Figure 4a above is an FTIR graph showing the absorbance over wavelength of the Zr-MOF. The spectrum shows the presence of a number of peaks. At the 543 cm^{-1} a ring in and out bending is observed, while at the 654 cm^{-1} position, a strong C-H bending is noticed. Moving along to the 743 cm^{-1} position, there is a weak C-C skeletal vibration. At the 1100 cm^{-1} position, there is a C-O stretch of variable strength. At the 1389 wavenumber, there is observed to be C-H aliphatic bending. At 1650 cm^{-1} there is a C-C aromatic stretch, and finally, at 3390 cm^{-1}, there is the presence of free O-H, signifying the presence of water molecules in the compound. Figure 4b below is the FTIR spectrum of BDA. When compared with Figure 4a, you observed that there were changes in the wavenumbers. This confirms that Zr-MOFs was produced.

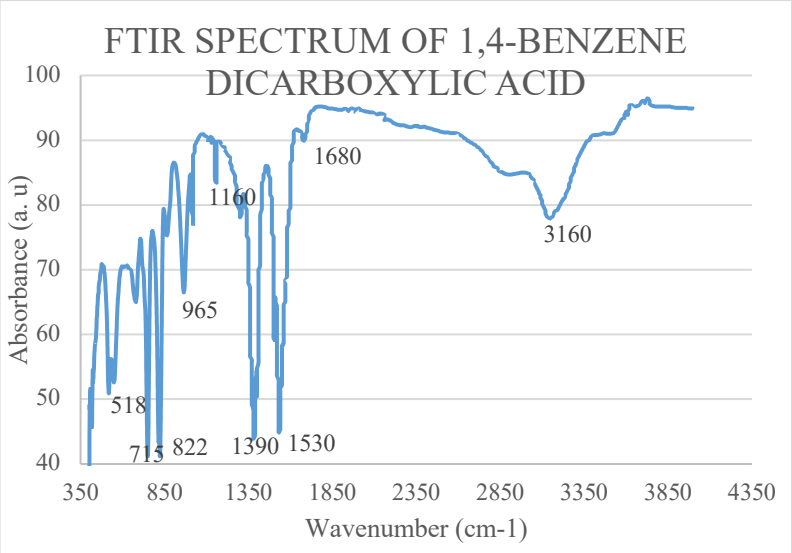

Figure 4b: FTIR spectrum of 1,4-Benzenedicarboxylic acid

The above graph is an FTIR graph in Figure 4b showing the absorbance against wavenumber of the benzene-1,4-dicarboxylic acid. This compound has a ring in and out plane bending at 518cm^{-1} and a C-H bending of medium to strong strength at 715cm^{-1}. At the 822cm^{-1} wavenumber, the same C-H bond is found to be present. At the 965cm^{-1}, there is a C-O stretch which is variable. At the 1160cm^{-1} point, there is still observed to be a C-O stretch. At 1390cm^{-1}, there is a C-H aliphatic bending. At the 1530cm^{-1} wavenumber, there is still a C-H bending present. At the 1680cm^{-1}, there is a C=C functional group present and at 3160cm^{-1}, there is a presence of O-H functional group which signifies the presence of water molecules in the compound.

In comparison between the two spectra, it is seen that a new peak is observed on the Zr-MOF spectrum diagram at 434cm^{-1}. The O-Metal bond which signifies that a new functional group has been formed.

Scanning Electron Microscopic (SEM) Spectrum

The surface morphology of the created metal-organic framework materials was examined using a scanning electron microscope. The SEM of the synthesized material is provided. The morphology of the crystals of Zirconium MOF showed several pores and irregular shapes.

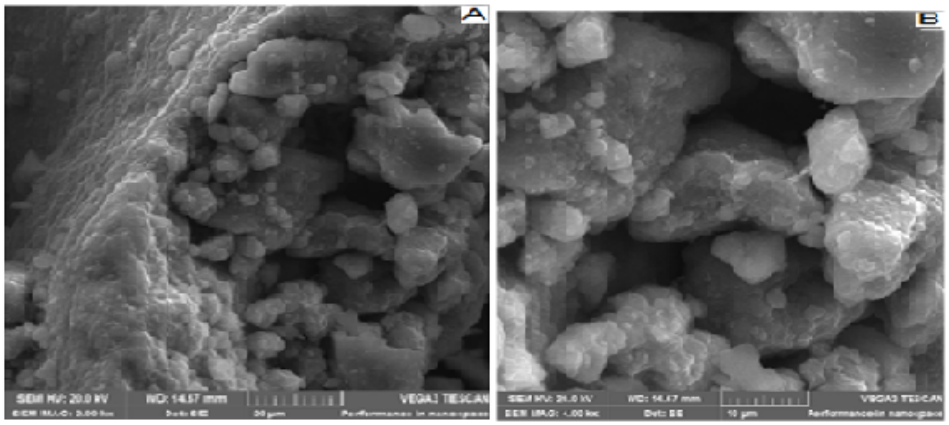

Figure 5: Scanning Electron Microscopic (SEM) Image for Zr-MOF. (A) x20 µm (B)x10 µm

Energy Dispersive X-Ray Spectroscopy (EDX)

Energy Dispersive X-ray spectroscopy (EDXS), a potent characterisation method, offers information on the metal elements present in the as-synthesized material, which is a direct pointer to the effective synthesis of the material and possibly the purity of the material as well. The EDXS of Zirconium MOF (Figure 6), shows the elements Zirconium, Zr, Carbon, Chlorine, and Oxygen only. The elemental composition of metals as revealed is given. Carbon C=54.5%, Oxygen O=22.5%, Zirconium Zr=18%, & Chlorine Cl=5.1%. The presence of the chlorine is a proof that chloride salts are not very soluble or it could be as a result of complex formation between the zirconium chloride and terephthalic acid. Zirconium has peaks at 2.3, 15.8 & 18.0 keV as a result of the isotopes which may be present. Oxygen peak is at 0.5keV, Chlorine peak is seen at 2.7keV. Carbon is at 0.1keV.

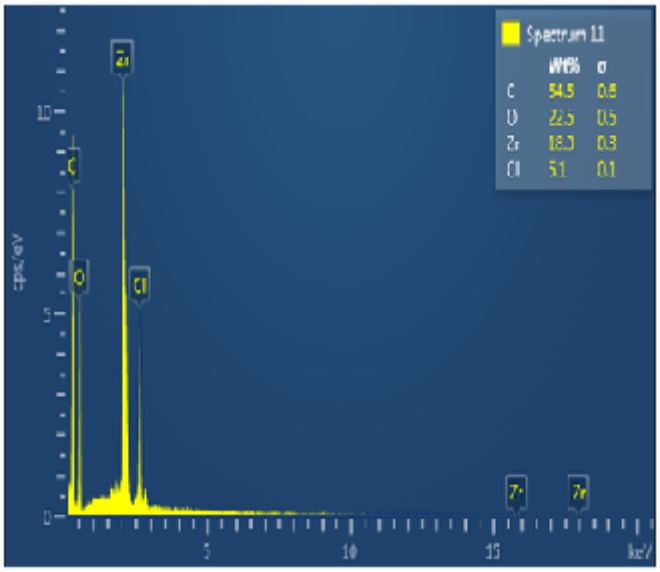

Figure 6: Energy Dispersive X-ray Spectroscopy(EDX) of Zirconium Metal Organic Framework (Zr-MOF) with Benzene-1,4-dicarboxylic acid (BDA) (Terephthalic acid) linker

Adsorption Result

Adsorption result for Zirconium Metal Organic Framework (Zr-MOF) or (Zr-BDA) of Benzene-1,4-dicarboxylic acid presented in Figure 7 showed that 0.2 g of the adsorbent adsorbed 20% of the crude oil while 0.4 g & 0.6 g adsorbed 30% each. 0.8 g adsorbed 50% and 1.0 g adsorbed 70%. Although the highest mass used for the sorption process, adsorbed seventy percent of the crude oil. The presence of chlorine in the MOF may have harmed the effectiveness of the Zr-MOF. Chlorine is negatively charged and may have influence the availability of positively charged ions from the zirconium metal. It is known that positive charged surfaces adsorb more of neutral molecules.

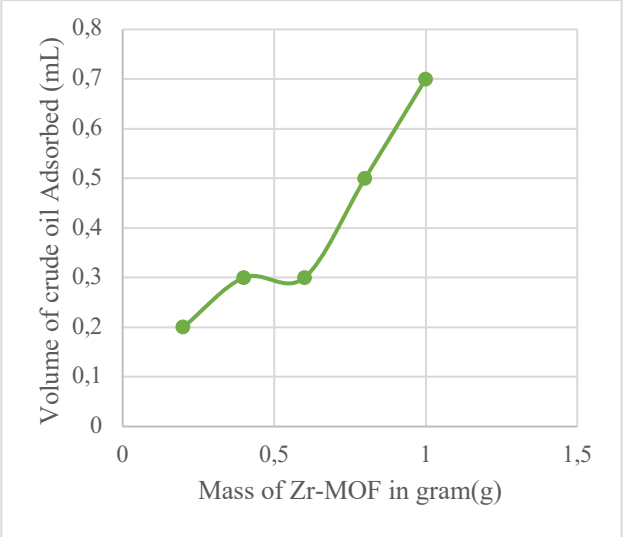

Figure 7: Adsorption graph for Zr-MOF

Composite Result for Adsorption of Crude Oil in Ratio 1:1

The results for the clay/MOF composites prepared and used for the analysis are presented below from Figure 8, and the term "composite" simply refers to the mixing of substances or materials in order to improve or modify their physical or chemical properties. Composite Zr-MOF/clay in ratio 1:1 adsorption results are presented in Figure 8. As a result of the figure presented, 0.2 g would have adsorbed nothing (zero adsorption). 0.6 g of Zr-MOF/clay adsorbed 20% and 0.8 g of Zr-MOF/clay adsorbed 30% of the crude oil. The performance was below expectations.

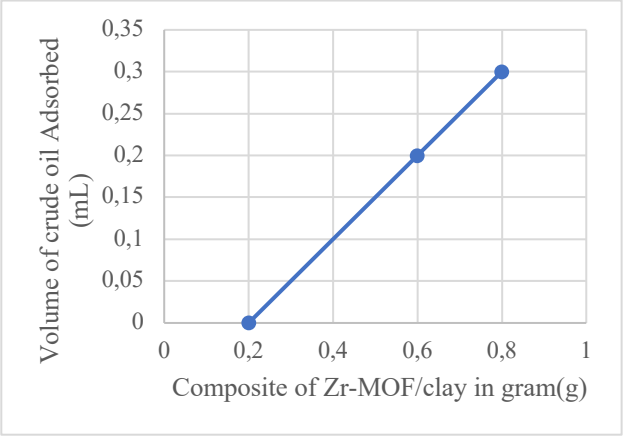

Figure 8: The adsorption of crude oil by composite of Zr-MOF/clay

Composite Result for Adsorption of Crude Oil in Ratio 1:1 with Charcoal

Figure 9 in this section displays the outcomes of the adsorption of crude oil by a composite made of a metal organic framework and charcoal. Figure 9 displays the composite Zr-MOF/charcoal adsorption findings at a ratio of 1:1. The outcome varied from 80% to 100%, excellent absorption.

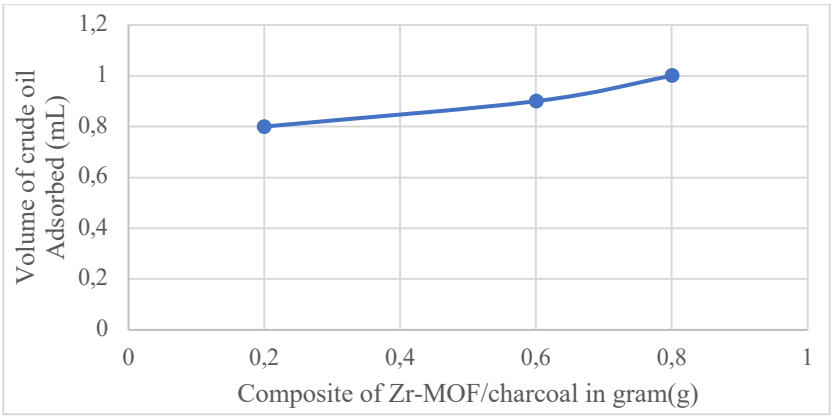

Figure 9: The graphical result of the composite of Zr-MOF and charcoal in grams (g)

Volume Concentration of Crude Oil in (mL)/1 g of the Adsorbent (Vol. of Crude Oil to Adsorbent Ratio)

The greatest amount of crude oil that the adsorbent could absorb was calculated in this study section. The amount of crude oil was increased to achieve this. The volume of the adsorbent was increased by 2 mL, 3 mL, and 4 mL while remaining constant at 1.0 g. Figure 10 presents the data that were obtained. Figure 10 displays the volume concentration of the crude oil in mL/1 g of Zr-MOF adsorption findings. 35% of 2 mL, 23.3% of 3 mL, and 20% of 4 mL of the crude oil were used. Based on the percentages discovered, 1.0 g of Zr-MOF is insufficient for a greater volume.

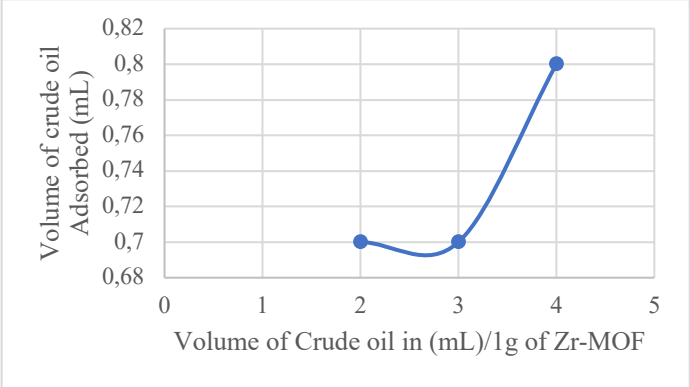

Figure 10: Volume concentration of crude oil in mL/1g of Zr-MOF & the quantity of crude oil that was adsorbed

pH Effect

The pH of the solution has an impact on the charge density of the adsorbent and adsorbate. Figure 11 illustrates how pH affects the adsorption of crude oil onto benzene-1,4-dicarboxylic acid-based organic zirconium metal framework materials. The effect of pH for Zr-MOF on adsorption capacity is presented in Figure 11. The curve increased and later slopped down. 90% of the crude oil was adsorbed at pH 4.4, 95% at pH 6.85, and 80% at pH 9.

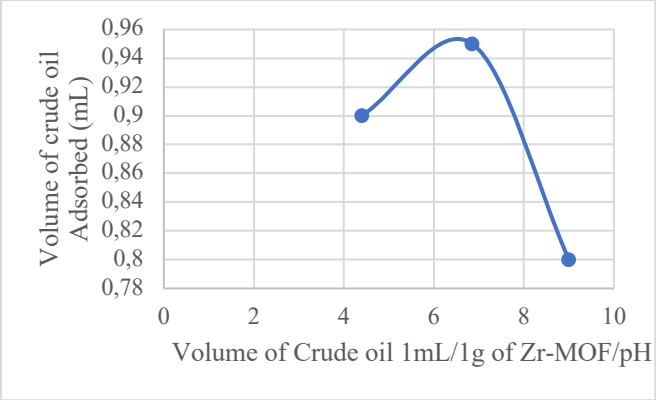

Figure 11: Result of pH effect on the adsorption property of Zr-MOF

CONCLUSION

The synthesis, characterization, and adsorption studies of zirconium and benzene-1,4-dicarboxylic acid was successfully carried out. The synthesis was carried out using the metal chloride salt and the organic ligand, then with the aid of dimethylformamide as the solvent for the reaction. The mixture was synthesized completely from start to finish in the span of three hours and characterized; characterization proved the formation of an MOF at the 434 cm^{-1} wavelength positions. It also proves that the compound is highly crystalline because of the multiple peaks. The adsorption study of Zr-MOF shows that it has an adsorption efficiency of 50%. It is therefore not a good adsorbent, as it has an efficiency of less than 80%. MOFs are a new and very important class of crystalline porous materials. This research has exposed some of the properties of the transition metal MOF, Zr-MOF. Ag-MOFs BDA, have been synthesized and utilized for crude oil remediation by Dikio, Abasi, and Orodu (2023), that display impeccable properties when compared with Zr-MOFs and would be very useful in the environment, especially in the area of crude oil clean-up. Although, the use of charcoal and pH improved the adsorption property of Zr-MOFs.

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